

# Syntheses, Structures and Characterizations of Two New Zinc(II) Coordination Polymers Constructed from 3-(1H-Pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole and Different Carboxylate Ligand

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**ABSTRACT** Two new zinc(II) coordination polymers,  $[\text{Zn}(\text{ph})(\text{H}_2\text{L})\cdot\text{H}_2\text{O}]_{2n}$  (**1**) and  $[\text{Zn}(\text{ip})(\text{H}_2\text{L})(\text{H}_2\text{O})]_n$  (**2**) ( $\text{H}_2\text{ph}$  = phthalic acid,  $\text{H}_2\text{ip}$  = isophthalic acid,  $\text{H}_2\text{L}$  = 3-(1H-pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole), have been successfully synthesized via hydrothermal reaction. It has been structurally characterized by X-ray single-crystal analysis, IR spectra, fluorescence spectroscopy and thermogravimetry analysis. The single-crystal X-ray diffraction studies reveal that compounds **1** and **2** both exhibit 1D chain structures, and assemble into 2D and 3D supermolecules through hydrogen bonds or  $\pi$ - $\pi$  interactions. Moreover, the thermal stability and luminescent properties of compounds **1** and **2** were also studied.

**Keywords:** zinc(II); coordination polymer; crystal structure; luminescent property;

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## 1 INTRODUCTION

In recent years, the coordination polymers have increasingly attracted considerable attention for their charming structures and potential applications in gas absorption and separation, luminescence, catalysis, molecular magnetism, sensors, *etc*<sup>[1-6]</sup>. Although many MOFs with various structures and properties have been synthesized in various ways and strategies over the past few decades, obtaining desirable frameworks with specific structures and functions is still a challenge because several key factors such as metal centers, organic

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ligands, reaction temperature, solvents, templates and pH may affect the self-assembly of coordination polymers<sup>[7]</sup>. Therefore, the most effective strategy for obtaining various functional coordination polymers is through the self-assembly of metal ions and multidentate organic ligands with two or more coordination atoms like N and O<sup>[8]</sup>. Significantly, mixed ligands incorporating N-donor ligands and multicarboxylates have been proven to be an effective strategy to construct intriguing coordination polymers. Hence, we selected 3-(1H-pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-triazole, phthalic acid and isophthalic acid as ligands (see Table 1), and two new complexes were obtained, namely,  $[\text{Zn}(\text{ph})(\text{H}_2\text{L})\text{H}_2\text{O}]_{2n}$  (**1**) and  $[\text{Zn}(\text{ip})(\text{H}_2\text{L})(\text{H}_2\text{O})]_n$  (**2**), and their luminescent properties in the solid state were explored at room temperature. Compounds **1** and **2** have different emission wavelength in comparison with the Zn(II)-L polymers.

## 2 EXPERIMENTAL

### 2.1 Materials and characterization

All the chemicals were commercially available and used without further purification. The X-ray single-crystal diffraction was put on a Rigaku oxford diffraction equipped with a graphite-monochromatic  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using the X-scan technique. The IR spectrum was recorded (3500~500  $\text{cm}^{-1}$  region) on an IRAffinity-1S (SHIMADZU) FT-IR Spectrometer. All fluorescence measurements were carried out on an F-7000 (HITACHI) Fluorescence Spectrophotometer (220~240 V). Thermogravimetric analyses (TGA) were performed in nitrogen at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  using a TG/DTA 6300 integration thermal analyzer. The X-ray powder diffraction patterns (XRPD) of compounds **1** and **2** were recorded at 293 K on a Bruker D8 Advance diffractometer ( $\text{CuK}\alpha$ ,  $\lambda = 1.54056 \text{ \AA}$ ) operated at 40 kV and 30 mA, using a Cu-target tube and a graphite-monochromator.

### 2.2 Preparation of compounds 1 and 2

A mixture of  $\text{H}_2\text{L}$  (21.2 mg, 0.10 mmol),  $\text{H}_2\text{hp}$  (33.2 mg, 0.20 mmol) and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (21.9 mg, 0.10 mmol) was dissolved in  $\text{H}_2\text{O}$  and put into a 10 mL small glass bottle. After stirring and sealing in a 25 mL Teflon-lined stainless-steel autoclave at  $135 \text{ }^\circ\text{C}$  for 96 h, then cooling to room temperature at a rate of  $5 \text{ }^\circ\text{C}\cdot\text{h}^{-1}$ , light yellow lump crystals were isolated and washed with distilled water, namely  $[\text{Zn}(\text{hp})(\text{H}_2\text{L})\text{H}_2\text{O}]_{2n}$  (**1**). IR ( $\text{cm}^{-1}$ ): 3398(w), 2980(w), 2881(w), 2355(m), 1570(m), 1384(m), 1145(m), 1040(m), 930(m), 830(m), 740(m).

A mixture of  $\text{H}_2\text{L}$  (21.2 mg, 0.10 mmol),  $\text{H}_2\text{ip}$  (33.2 mg, 0.20 mmol) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (89.1 mg, 0.30 mmol) was dissolved in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (v:v = 1: 4 mL) and put into a 10 mL small glass bottle. After stirring

and sealing in a 25 mL Teflon-lined stainless-steel autoclave at 135 °C for 72 h, and cooling to room temperature at a rate of 5 °C·h<sup>-1</sup>, colourless lump crystals were isolated and washed with distilled water, namely [Zn(ip)(H<sub>2</sub>L)(H<sub>2</sub>O)]<sub>n</sub> (**2**). IR(cm<sup>-1</sup>): 3271(w), 3127(w), 2974(w), 2365(m), 1630(m), 1546(m), 1457(m), 1357(m), 1150(m), 1052(m), 927(m), 720(m).

### 2.3 X-ray crystallography

Singles crystals of **1** and **2** were put on a Rigaku oxford diffraction equipped with a graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using X-scan technique. Empirical absorption corrections were made using the SADABS program<sup>[9]</sup>. The structure was solved by direct methods using SHELXS-97<sup>[10]</sup> and refined on  $F^2$  by full-matrix least-squares with SHELXL-97<sup>[11]</sup>. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. Crystallographic data for **1** and **2** are listed in Table 2, and their selected bond lengths and bond angles are respectively given in Tables 3 and 4. Hydrogen bonds for compounds **1** and **2** are shown in Table 5.

## 3 RESULTS AND DISCUSSION

### 3.1 IR spectroscopy

In the IR spectra of **1** and **2**, the IR spectrum also shows a weak broad characteristic peak of N–H of H<sub>2</sub>L ligand and O–H or C–H stretching vibrations of the aromatic rings at 2281~3398 and 2974~3271 cm<sup>-1</sup>. At the same time, the medium intense vibration bands at 2355 and 2365 cm<sup>-1</sup> are due to the Zn–O and Zn–N stretching vibrations. In addition, the characteristic bands of coordinated carboxylate groups appear at 1570~1384 and 1630~1357 cm<sup>-1</sup>, whereas the out-of-plane bending vibrations of aromatic rings are observed at 1145~740 and 1150~720 cm<sup>-1</sup>. Therefore, the IR spectra analysis has a good agreement with the X-ray single-crystal structure and previous report<sup>[5, 12-15]</sup>.

### 3.2 Crystal structure description of **1** and **2**

X-ray single-crystal diffraction analysis reveals that **1** crystallizes in orthorhombic system, space group  $P2_12_12_1$  and exhibits a 1D chain structure. The coordination environment of Zn(II) in **1** is shown in Fig. 1a. The asymmetric unit consists of two crystallographically independent Zn(II) ions, two H<sub>2</sub>L<sup>-</sup> ligands, two ph<sup>2-</sup> ligands and two free water molecules. Two Zn(II) ions in **1** are both five-coordinated, in which the Zn1 ion is coordinated by three nitrogen atoms (N(1), N(2), N(5)<sup>#1</sup>) of two different H<sub>2</sub>L ligands and two oxygen atoms

(O(1) and O(4)<sup>#1</sup>) from two different H<sub>2</sub>bdc ligands, and the Zn(2) ion is coordinated by three nitrogen atoms (N(7)<sup>#3</sup>, N(10)<sup>#3</sup>, N(12)) of two different H<sub>2</sub>L ligands and two oxygen atoms (O(5) and O(8)<sup>#2</sup>) from two different H<sub>2</sub>bdc ligands. The Zn–O and Zn–N distances respectively locate in the ranges of 1.970(6)~2.033(6) and 2.128(8)~2.197(7) Å, which are quite in agreement with the bond distances reported for similar complexes in literature<sup>[16-18]</sup>. In Fig. 1b, the H<sub>2</sub>L ligand as a bridging ligand is connected with two Zn(II) ions through the imidazole N atom, the pyridine adjacent N atoms and the pyrazole N atom. At the same time, two adjacent Zn(II) ions are bridged by one carboxylate group atom from the H<sub>2</sub>ph ligand. Finally, a one-dimensional helical double-chain is generated along the *xy* plane<sup>[19]</sup>. Moreover, it is notable that complex **1** involves abundant intramolecular and intermolecular hydrogen bonds, as a result of the intermolecular hydrogen bonds between the carboxylate group oxygen atom of H<sub>2</sub>ph and the pyrazole N atom of H<sub>2</sub>L (N(5)–H(5)···O(4), N(5)–H(5)···O(1)). There are intramolecular hydrogen bonds between the carboxylate group oxygen atom of H<sub>2</sub>ph and the imidazole N atom of H<sub>2</sub>L (N(4)–H(4)···O(7)), between free water and the imidazole N atom of H<sub>2</sub>L (N(9)–H(9)···O(9)), and also between free water and the carboxylate group oxygen atom of H<sub>2</sub>ph (O(9)–H(9A)···O(3), O(9)–H(9B)···O(4), O(9)–H(10A)···O(8)). Thereby, complex **1** can be viewed as a two-dimensional supramolecular architecture further extended via these hydrogen bonds that may enhance its structural stability<sup>[20]</sup> (Fig. 1c).

X-ray single-crystal structural analysis reveals that compound **2** crystallizes in monoclinic system, space group *P*2<sub>1</sub>/*n* and features a 1D chain structure. The coordination environment of Zn(II) in **2** is shown in Fig. 2a. The asymmetric unit of **2** contains one Zn(II) ion, one H<sub>2</sub>L ligand, one ip<sup>2-</sup> ligand and one coordinate water molecule. As shown in Fig. 2a, the Zn(II) ion in **2** is five-coordinated, which is defined by two oxygen atoms (O(2) and O(5)<sup>#1</sup>) from two different H<sub>2</sub>ipa ligands, one oxygen atom (O(1)) from one coordinate water molecule and two nitrogen atoms (N(1) and N(2)) from one H<sub>2</sub>L ligand. These bond angles and bond distances all fall in the normal ranges<sup>[16-18]</sup>, such as the Zn–O and Zn–N distances falling in the ranges of 2.006(2)~2.189(2) and 2.091(2)~2.172(2) Å. In Fig. 2b, two Zn(II) ions are bridged by the imidazole N atom and the pyridine adjacent N atoms of one H<sub>2</sub>L ligand as a terminal ligand to form planar units, which are further bridged by one carboxylic oxygen atom of one isophthalic acid as a bridging ligand to finally give rise to a chain structure along the *yz* plane (Fig. 2b). Owing to the introduction of coordinate water molecules, complex **2** has not only intramolecular but also intermolecular hydrogen bonds. As a result of the intermolecular hydrogen bonds between the coordinate water and carboxylate group oxygen atom of H<sub>2</sub>ip (O(1)–H(1B)···O(3), O(1)–H(1B)···O(5)), intermolecular hydrogen bonds appear between the carboxylate group oxygen atom of

H<sub>2</sub>L and the imidazole N atom and pyrazole N atom of H<sub>2</sub>L (N(4)–H(4)···O(4), N(5)–H(5)···O(3)). Notably, there are  $\pi$ - $\pi$  stacking interactions in complex **2**, with the distance to be 3.699 Å. These hydrogen bonds and  $\pi$ - $\pi$  stacking interactions in **2** affect the stability of the structure, finally generating a 3D supramolecular architecture (Fig. 2c).

From the above structural analyses, we can see clearly that different dicarboxylates show synergistic effects on the diverse structures of the title complexes. The carboxyl groups of dicarboxylates exhibit a bis(monodentate) bridging mode  $\mu_1$ - $\eta^1$ : $\eta^0$  to link two Zn(II) ions, and the Zn(II) ions are also five-coordinated and display slightly distorted square pyramidal geometry in compounds **1** and **2**. However, in complex **1**, the H<sub>2</sub>L ligand adopts the  $\mu_2$ -bridging + chelating modes to bind two Zn(II) atoms, which involves abundant hydrogen bonds, and finally forms a 2D layer structure. Different from that in complex **1**, in compound **2**, the H<sub>2</sub>L ligands adopts a  $\mu_1$ -chelating mode to link one Zn(II) atom (Table 1), which has not only hydrogen bonds but also  $\pi$ - $\pi$  stacking interactions, and generates a 3D network structure.

### 3.3 XRD analyses

In order to check whether the crystal structures are truly representative of the bulk materials, powder X-ray diffraction (PXRD) experiments were carried out for **1** and **2** at room temperature. As shown in Fig. 3, the peak positions of simulated and experimental PXRD patterns are in agreement with each other, demonstrating that the bulk synthesized materials and the measured single crystals are the same.

### 3.4 Thermogravimetric analyses

The thermal stabilities of complexes **1** and **2** were tested in the range of 20~800 °C under a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup> for a TG/DTA 6300 integration thermal analyzer. The TGA curves of complexes **1** and **2** are shown in Fig. 4. The thermogram follows the decrease in sample weight with the linear increase in heat treatment temperature (10 °C min<sup>-1</sup>) up to 800 °C. The thermal gravimetric analysis curves show that complex **1** undergoes two main weight loss steps. The first one below 165 °C is attributed to the release of two uncoordinated water molecules per unit cell (observed 3.11%, calculated 3.93%), and then the desolvated samples can be stable up to 285 °C. After that, rapid weight loss can be observed owing to the decomposition of the framework, while the polymeric framework of **1** has started to decompose slowly after the temperature increases to about 310 °C. For complex **2**, the quality of the sample is gradually slowly lost with the increase of temperature before 310 °C, which is attributed to the departure of one coordinated water molecule per unit cell (observed 4.97%, calculated 3.92%). The small difference between the experimental and calculated values may be ascribed to the sample with many adsorbed solvents on the crystal surface. After that,

faster weight loss can be observed owing to the decomposition of the framework. The last same residues of compounds **1** and **2** may be both ZnO (observed 20.05%, calculated 17.78%; observed 18.91%, calculated 17.70%) and unburned carbon. The results suggest that the backbone of **2** is more thermally robust than **1**, and can resist decomposition up to 310 °C.

### 3.5 Photoluminescent properties

The solid-state luminescent properties of the as-synthesized samples **1** and **2** and free ligand are measured at room temperature and the same conditions (slit width = 2.5 nm, lamp voltage = 700 V). As shown in Fig. 5, the free ligands H<sub>2</sub>L, H<sub>2</sub>ph and H<sub>2</sub>ip display photoluminescence with emission maxima at 380 nm ( $\lambda_{\text{ex}} = 325$  nm), 343 nm ( $\lambda_{\text{ex}} = 312$  nm) and 392 nm ( $\lambda_{\text{ex}} = 350$  nm), which are probably derived from the  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions<sup>[21]</sup>. For complexes **1** and **2**, the emission peaks at 408 ( $\lambda_{\text{ex}} = 325$  nm) and 418 nm ( $\lambda_{\text{ex}} = 330$  nm) are found, which is red-shifted by 28 and 38 nm as compared with the free H<sub>2</sub>L ligand. The red-shifted phenomena should be best ascribed to the metal-to-ligand charge transfer according to literatures<sup>[22, 23]</sup>, in which the red shift may be derived from the different coordination fashions of organic ligands, different architectures and components<sup>[24]</sup>.

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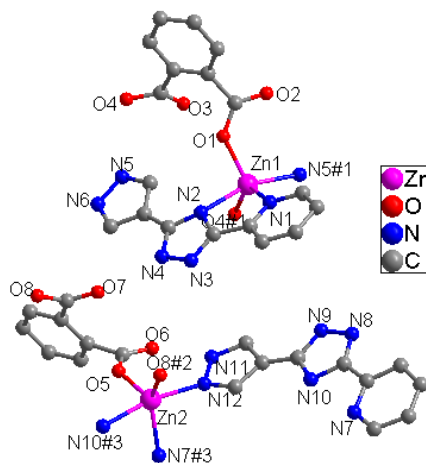
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**Fig. 1a. Coordination environment of Zn(II) in 1**





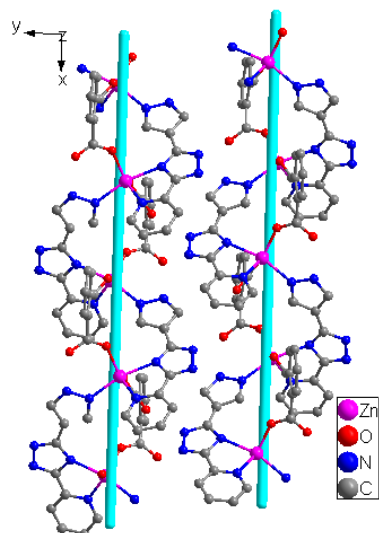


Fig. 1b. A 1D one-dimensional helical double-chain of 1

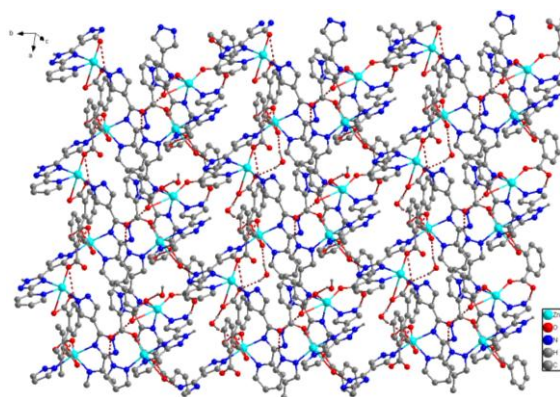


Fig. 1c. A 2D structure (*c*-axis) connected by hydrogen bonds of 1

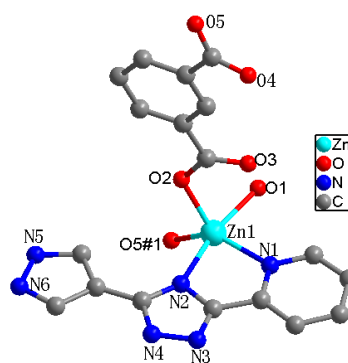


Fig. 2a. Coordination environment of Zn(II) in 2

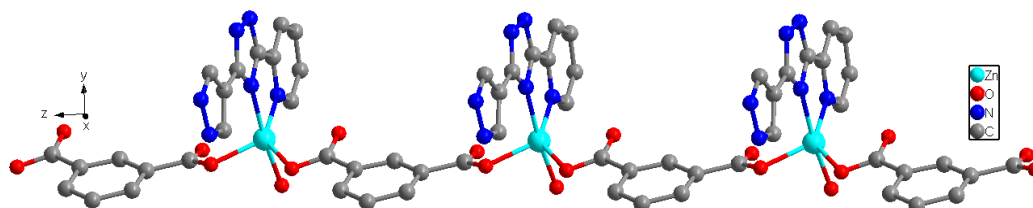


Fig. 2b. A 1D one-dimensional chain structure of 2



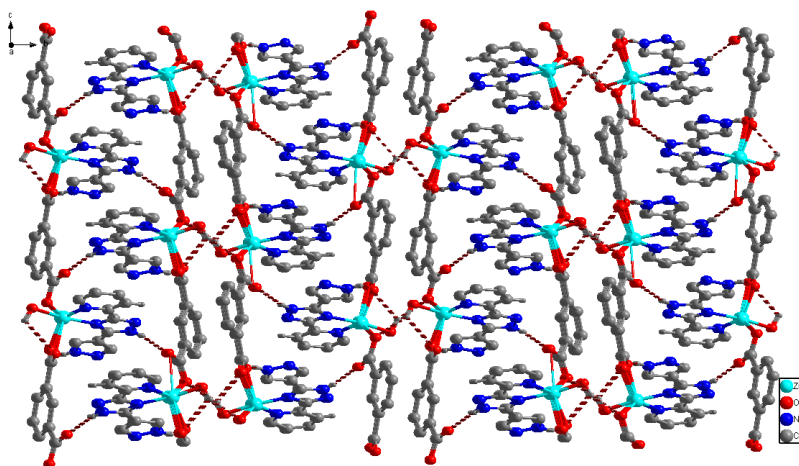


Fig. 2c. A 3D structure (*c*-axis) connected by hydrogen bonds and  $\pi \cdots \pi$  interactions of 2

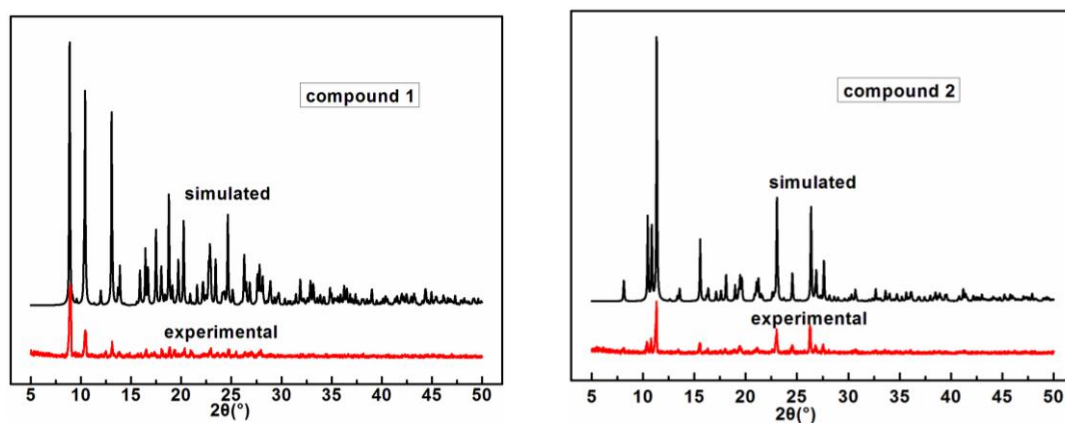


Fig. 3. PXRD patterns of compounds 1 and 2

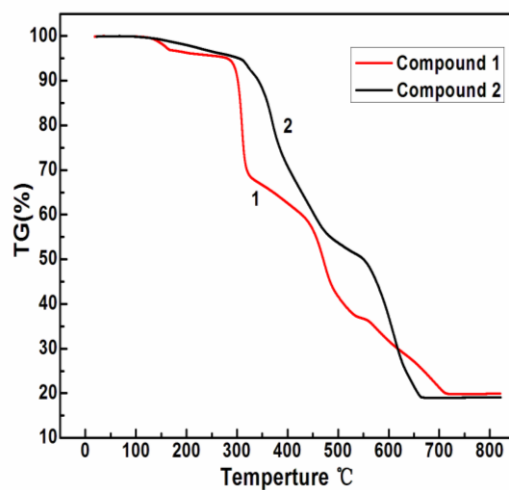


Fig. 4. TGA curves of compounds 1 and 2

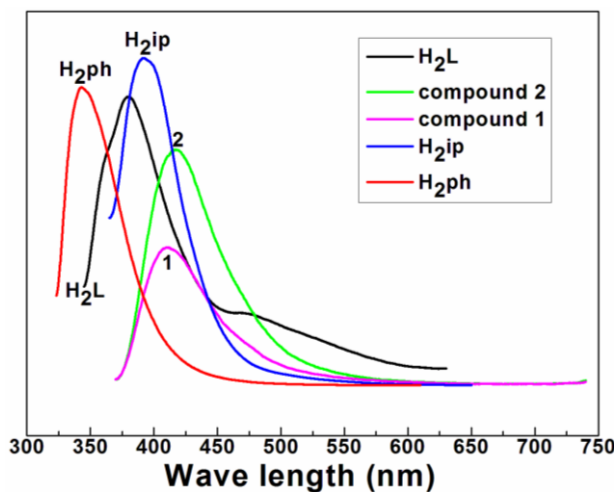


Fig. 5. Fluorescence in the solid state of H<sub>2</sub>L, H<sub>2</sub>hp, H<sub>2</sub>ip and 1 and 2

| Table 1. Coordination Modes of Zn(II) and the Ligand in Compounds |             |                  |                |
|---|-------------|------------------|----------------|
| Compounds   | Zn(II) atom | H <sub>2</sub> L | Dicarboxylates |
| 1   |             |                  |                |
| 2   |             |                  |                |

| Table 2. Crystallographic Data of Compounds 1 and 2 |   |  |
|---|---|--|
| Compound  | 1   | 2  |
| Empirical formula                                   | C <sub>36</sub> H <sub>28</sub> N <sub>12</sub> O <sub>10</sub> Zn <sub>2</sub> | C <sub>18</sub> H <sub>14</sub> N <sub>6</sub> O <sub>5</sub> Zn |
| Formula weight                                      | 919.44  | 459.72   |
| Temperature/K                                       | 288.75(10)  | 293(2)   |
| Crystal system                                      | Orthorhombic  | Monoclinic   |
| Space group   | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                           | <i>P</i> 2 <sub>1</sub> / <i>n</i>                               |
| <i>a</i> /Å   | 11.0162(7)  | 9.2495(6)  |
| <i>b</i> /Å   | 16.9914(15)   | 21.7422(11)  |
| <i>c</i> /Å   | 19.9185(16)   | 10.1578(8)   |
| <i>α</i> /°   | 90  | 90   |
| <i>β</i> /°   | 90  | 115.303(10)  |
| <i>γ</i> /°   | 90  | 90   |
| <i>V</i> /Å <sup>3</sup>                            | 3728.4(5)   | 1846.8(3)  |

|  |  |   |
|--|--|---|
| Z  | 4  | 4   |
| $D_c$  | 1.638  | 1.653   |
| $\mu/\text{mm}^{-1}$                                       | 1.364  | 1.377   |
| $F(000)$   | 1872.0   | 936.0   |
| $2\theta$ range for data collection/ $^\circ$              | 7.166 to 50.998  | 7.162 to 55.932   |
| Index ranges   | $-8 \leq h \leq 13$ ; $-20 \leq k \leq 14$ ;<br>$-21 \leq l \leq 24$ | $-11 \leq h \leq 11$ ; $-25 \leq k \leq 28$ ;<br>$-10 \leq l \leq 13$ |
| Reflections collected                                      | 10958  | 10327   |
| Independent reflections                                    | 6474 ( $R_{\text{int}} = 0.0466$ )                                   | 3687 ( $R_{\text{int}} = 0.0241$ )                                    |
| Data/restraints/parameters                                 | 6474/0/555   | 3687/0/272  |
| Goodness-of-fit on $F^2$                                   | 1.026  | 1.070   |
| Final $R$ indexes ( $I > 2\sigma(I)$ )                     | $R = 0.0647$ , $wR = 0.1232$   | $R = 0.0418$ , $wR = 0.0914$  |
| Final $R$ indexes (all data)                               | $R = 0.0939$ , $wR = 0.1379$   | $R = 0.0528$ , $wR = 0.0964$  |
| Largest diff. peak/hole / $\text{e} \cdot \text{\AA}^{-3}$ | 0.79/−0.75   | 0.56/−0.49  |

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) of Compound 1

| Bond   | Dist.    | Bond  | Dist.    |
|--|----------|---|----------|
| Zn(1)–O(4) <sup>#1</sup>                     | 2.024(6) | Zn(2)–N(7) <sup>#4</sup>                      | 2.137(8) |
| Zn(1)–O(1)                                   | 1.972(6) | Zn(2)–N(12)                                   | 2.119(8) |
| Zn(1)–N(2)                                   | 2.192(7) | Zn(2)–O(5)                                    | 1.985(7) |
| Zn(1)–N(5) <sup>#1</sup>                     | 2.168(8) | Zn(2)–O(8) <sup>#3</sup>                      | 2.035(6) |
| Zn(1)–N(1)                                   | 2.123(8) | Zn(2)–N(10) <sup>#4</sup>                     | 2.172(7) |
| Angle  | (°)      | Angle   | (°)      |
| O(4) <sup>1</sup> –Zn(1)–N(2)                | 85.8(3)  | N(12)–Zn(2)–N(10) <sup>#4</sup>               | 165.8(3) |
| O(4) <sup>#1</sup> –Zn(1)–N(5) <sup>#1</sup> | 86.9(3)  | N(12)–Zn(2)–N(7) <sup>#4</sup>                | 93.1(3)  |
| O(4) <sup>#1</sup> –Zn(1)–N(1)               | 129.6(3) | O(1)–Zn(1)–N(5) <sup>#1</sup>                 | 104.5(3) |
| O(1)–Zn(1)–O(4) <sup>#1</sup>                | 112.5(3) | O(1)–Zn(1)–N(1)                               | 115.3(3) |
| O(1)–Zn(1)–N(2)                              | 93.4(3)  | N(5) <sup>#1</sup> –Zn(1)–N(2)                | 162.0(3) |
| N(1)–Zn(1)–N(2)                              | 76.6(3)  | N(6)–N(5)–Zn(1) <sup>#2</sup>                 | 125.8(7) |
| N(1)–Zn(1)–N(5) <sup>#1</sup>                | 95.7(3)  | N(11)–N12–Zn(2)                               | 125.6(6) |
| O(5)–Zn(2)–O(8) <sup>#3</sup>                | 114.9(3) | O(8) <sup>#3</sup> –Zn(2)–N(10) <sup>#4</sup> | 88.8(3)  |
| O(5)–Zn(2)–N(10) <sup>#4</sup>               | 91.2(3)  | O(8) <sup>#3</sup> –Zn(2)–N(7) <sup>#4</sup>  | 128.7(3) |
| O(5)–Zn(2)–N(7) <sup>#4</sup>                | 114.6(3) | O(8) <sup>#3</sup> –Zn(2)–N(12)               | 88.8(3)  |
| O(5)–Zn(2)–N(12)                             | 102.5(3) | N(7) <sup>#4</sup> –Zn(2)–N(10) <sup>#4</sup> | 77.6(3)  |

Symmetry codes: <sup>#1</sup> 1/2+x, 1/2–y, 1–z; <sup>#2</sup> –1/2+x, 1/2–y, 1–z; <sup>#3</sup> 1/2+x, 3/2–y, 1–z; <sup>#4</sup> –1/2+x, 3/2–y, 1–z

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) of Compound 2

| Bond                     | Dist.    | Bond       | Dist.    |
|--------------------------|----------|------------|----------|
| Zn(1)–O(1)               | 2.189(2) | Zn(1)–N(1) | 2.090(2) |
| Zn(1)–O(2)               | 2.007(2) | Zn(1)–N(2) | 2.172(2) |
| Zn(1)–O(5) <sup>#1</sup> | 2.039(2) |            |          |
| Angle                    | (°)      | Angle      | (°)      |

|                                |           |                                |           |
|--------------------------------|-----------|--------------------------------|-----------|
| O(2)–Zn(1)–O(1)                | 90.89(9)  | N(1)–Zn(1)–N(2)                | 78.88(9)  |
| O(2)–Zn(1)–O(5) <sup>#1</sup>  | 96.73(9)  | N(2)–Zn(1)–O(1)                | 169.38(8) |
| O(2)–Zn(1)–N(1)                | 124.72(9) | O(5) <sup>#1</sup> –Zn(1)–N(1) | 138.49(9) |
| O(2)–Zn(1)–N(2)                | 96.16(9)  | O(5) <sup>#1</sup> –Zn(1)–N(2) | 96.23(9)  |
| O(5) <sup>#1</sup> –Zn(1)–O(1) | 90.80(8)  | N(1)–Zn(1)–O(1)                | 90.58(9)  |

Symmetry code: (1) x, y, –1+z

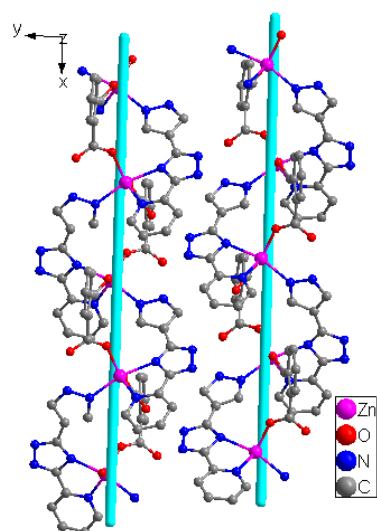
Table 5. Hydrogen Bond Lengths (Å) and Bond Angles ( ° ) of Compounds 1 and 2

| 1                                 |         |          |           |        |
|-----------------------------------|---------|----------|-----------|--------|
| D–H...A                           | d(D–H)  | d(H...A) | d(D...A)  | ∠DHA   |
| N(4)–H(4)...O(7)                  | 0.86    | 1.88     | 2.718(10) | 163.6  |
| N(11)–H(11A)...O(6)               | 0.86    | 1.83     | 2.632(11) | 153.5  |
| N(9)–H(9)...O(9)                  | 0.94(8) | 1.73(8)  | 2.666(10) | 171(7) |
| O(9)–H(9A)...O(3) <sup>#1</sup>   | 0.96    | 1.81     | 2.751(9)  | 164.8  |
| O(9)–H(9B)...O(4) <sup>#2</sup>   | 0.85    | 1.93     | 2.757(9)  | 163.1  |
| O(10)–H(10A)...O(8) <sup>#3</sup> | 0.85    | 1.99     | 2.837(13) | 178.2  |
| O(10)–H(10B)...N(3)               | 0.85    | 2.00     | 2.846(13) | 171.6  |
| 2                                 |         |          |           |        |
| O(1)–H(1B)...O(5) <sup>#1</sup>   | 0.86    | 2.11     | 2.864(3)  | 146.0  |
| N(4)–H(4)...O(4) <sup>#2</sup>    | 0.86    | 1.96     | 2.792(4)  | 162.8  |
| N(5)–H(5)...O(3) <sup>#3</sup>    | 0.86    | 2.09     | 2.780(4)  | 137.3  |

Symmetry codes: <sup>#1</sup>1/2+x, 1/2–y, 1–z; <sup>#2</sup>1+x, y, z; <sup>#3</sup>1/2+x, 3/2–y, 1–z for **1**; <sup>#1</sup>1–x, 1–y, 1–z; <sup>#2</sup>1/2+x, 3/2–y, –1/2+z; <sup>#3</sup>1+x, y, z for **2**

Syntheses, Structures and Characterizations of Two  
New Zinc(II) Coordination Polymers Constructed  
from 3-(1H-Pyrazol-4-yl)-5-(pyridin-2-yl)-1,2,4-  
triazole and Different Carboxylate Ligands

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Two new zinc(II) coordination polymers have been successfully synthesized via hydrothermal reaction. It has been structurally characterized by X-ray single-crystal analysis, IR spectra, fluorescence spectroscopy and thermogravimetry analysis. Compounds **1** and **2** both exhibit 1D chain structures, and assemble into 2D and 3D supramolecules through hydrogen bonds or  $\pi$ - $\pi$  interactions. Thermal stability and luminescent property of compounds **1** and **2** were also studied.